

Docket No.: 0315-0158PUS1  
(PATENT)

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Patent Application of:  
Antonio Luiz Duarte BRAGANCA et al.

Application No.: 10/518,443

Confirmation No.: 7833

Filed: July 1, 2005

Art Unit: 1793

For: SOLID CATALYST COMPONENT FOR  
POLYMERIZATION AND  
COPOLYMERIZATION OF ETHYLENE,  
AND, PROCESS FOR OBTAINING THE  
SAME

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Examiner: J. E. McDonough

**REPLY BRIEF UNDER 37 C.F.R. § 41.41**

MS Appeal Brief - Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

June 30, 2009

Madam:

In reply to the Examiner's Answer dated May 1, 2009, the following remarks are respectfully submitted in connection with the above-identified application.

Remarks begin on page 2.

### REMARKS

The present invention defines a unique catalyst composition which contains specific amounts of catalytically active components, that is, specific amounts of Ti, Mg and Cl, which when used in a polymerization process produces homopolymers and/or copolymers of either High Density Polyethylene (HDPE) or Linear Low Density Polyethylene (LLDPE) with a controlled morphology, having one or more of the following properties, that is, high bulk density, a very small quantity of fines in the product, good co-monomer insertion, improved catalytic activity with low catalytic decay and a substantial homogeneous distribution of the  $\alpha$ -olefin within the polymer chain in connection with LLDPE.

In rejecting the claims of the present application, the Examiner has relied upon Luciani et al., EP 0480435 (hereinafter referred to as Luciani I), Luciani et al., EP 0522651 (hereinafter referred to as Luciani II) and WO 91108239 (hereinafter referred to as Neste). The Table below compares the amounts of Ti, Mg and Cl present in the catalyst system of the present invention with that of Luciani I, Luciani II and Neste.

TABLE – Elemental ranges

	Present Application	EP 0480435 B1 Luciani I	EP0522651 B1 Luciani II	WO91/08239 Neste
Ti range (% w/w)	0.5 - 2.0	3.9 – 4.5 (outside)	3.7 – 4.4 (outside)	3.2 – 4.9 (outside)
Mg range (% w/w)	0.3 - 3.0  0.3 – 1.5 (pref)	2.7 – 5.0 (barely inside) (outside)	3.4 – 3.9 (outside)	0.70 – 1.75 (inside)
Cl range (% w/w)	5.0 - 12.0	17.7 – 21.0 (outside)	12.4 – 19.7 (outside)	12.2 – 22.5 (outside)
TOTAL (% w/w)	5.8 – 17.0	24.3 – 30.5 (outside)	19.5 – 28.0 (outside)	16.1 – 29.15 (barely inside)

As can be readily observed by referring to Table 1 above, none of the references relied upon by the Examiner contemplate the specific ranges of Ti, Mg and Cl as defined by the present invention. Thus, when referring to Luciani I, two of the three components

of the Appellants' catalyst system falls outside of the Appellants' range with the total thereof falling outside of the Applicants' range. In connection with Luciani II, all three of the relevant components including the total thereof fall outside of the Appellants' range and in connection with the Neste reference two of the three components of the Appellants' catalyst system fall outside of the Appellants' range with the total thereof falling barely inside the Appellants' range. Clearly, none of the prior art references relied upon by the Examiner disclose the Appellants' catalyst composition and for all of the reasons discussed in the Appellants' Appeal Brief, cannot achieve homopolymers and/or copolymers of either high density polyethylene or linear low density polyethylene with all of the properties referred to hereinabove.

In the "Response to Arguments" as presented in the Examiner's Answer, the Examiner dismisses many of the arguments provided by the Appellants and many of the results shown in the Declarations by taking the position that such showings are not pervasive because the Appellants have failed to compare the closest prior art. In all cases, the Appellants compares examples of the present application with examples in the prior art. It has long been understood that examples presented in the prior art are clearly most indicative of what the prior art considers to be the most enabling aspects of the invention as described in the patent. Accordingly, it is believed that comparing the examples of the present invention with examples in the prior art represents the best possible comparison to point out the relevant distinctions between the present invention and the prior art relied upon by the Examiner.

In addition to the above comments, the Appellants are further providing a summary of all of the comments already presented with a further analysis in order to corroborate what has already been submitted, for the Examiner's consideration.

Although the catalysts of the present invention and the catalysts of the prior art have the same elements in its composition (Ti, Mg, Si, Al) and the Examiner argues that it is not possible to distinguish the catalyst products of the present application from those of Luciani I and Luciani II, it is important to note that the processes for producing the

catalysts are not comparable and the present invention differs from these prior art references for the following reasons:

- Feature 1:** the organometallic compound, which in Luciani II is also the chlorinating agent, is impregnated into the support separately in step (a) and an additional halogenating (chlorinating) agent is employed in step (f).
- Feature 2:** the ratio of the amount of silica support to catalyst component used;
- Feature 3:** the ratio of the amount of silica support hydroxyl groups to organometallic component(s) used and the nature of said components;
- Feature 4:** the ratio of the amount of silica to magnesium component used;
- Feature 5:** a reducing agent is present;
- Feature 6:** no additional  $\text{TiCl}_4$  is employed;
- Feature 7:** the organic solvent used during the impregnation of the activated silica is non-polar;
- Feature 8:** the supernatant liquid from step (a) is removed by means of settling, siphoning, filtration or centrifugation (Luciani II makes use of evaporation);
- Feature 9:** an additional washing step is employed (step (h));
- Feature 10:** no electron donor is used during catalyst preparation (both Luciani I and Luciani II makes use of such electron donor compounds)

Analyses have been carried out, such as X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy, of the catalysts from example 8 of the present application and from example 3 of Luciani I and example 1 of Luciani II, with the objective to show that, despite all the similarities in the compositions of these catalysts (the catalysts have the same elements), they are different in their crystal structure and distribution form on the catalytic support.

It is evident, upon comparing the process for preparing the catalyst of the present invention and the processes for preparing the catalysts claimed in Luciani I and Luciani II, that the processes are different from each other since the processes claimed in Luciani I and Luciani II use electron donors as part of the catalyst preparation.

When an electron donor is used during the process of catalyst preparation, the magnesium and titanium compounds, which have been deposited on the catalytic support (silica), show crystalline structure modified with the presence of this donor.

According to studies from Mori *et al.* [ref. 1] which investigated the nature of titanium species from different Ziegler-Natta catalysts by X-ray photoelectron spectroscopy, the internal donor affects the nature of the active sites because it changes the environment through the interaction of this donor with  $\text{MgCl}_2$ , for example. According to Figure 2 which illustrates Table 2 of ref. 1, Ziegler-Natta catalysts with and without donors, showed Ti 2p<sub>3/2</sub> signal with the FWHM (full width at half maximum intensity) between 2.9 and 3.0 eV. It is important to say that FWHM represents the heterogeneity of titanium species: the larger the width of this signal, the more heterogeneous is the species in these catalysts. After treatment with TEAL, the FWHM increased, as shown in Figure 2 which illustrates Figure 1 from ref. 1.

Table 2			
XPS data of the $\text{Ti}_{2p_{3/2}}$ level in the supported catalysts and $\text{TiCl}_4$ -ester complexes			
Run No.	Catalyst	Binding energy <sup>a</sup> (eV)	FWHM <sup>b</sup> (eV)
1	$\text{TiCl}_4/\text{EB}/\text{MgCl}_2$	458.8	3.0
2	$\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$	458.9	3.1
3	$\text{TiCl}_4/\text{MgCl}_2$	458.9	2.9
4	$\text{TiCl}_4$ -EB complex	459.1	2.4
5	$\text{TiCl}_4$ -DBP complex	459.2	2.4

<sup>a</sup>Reference:  $\text{Au}_{4f_{7/2}}$  (84.0 eV).  
<sup>b</sup>Full width at half maximum intensity.

FIGURE 1 – Table 2 from ref. 1

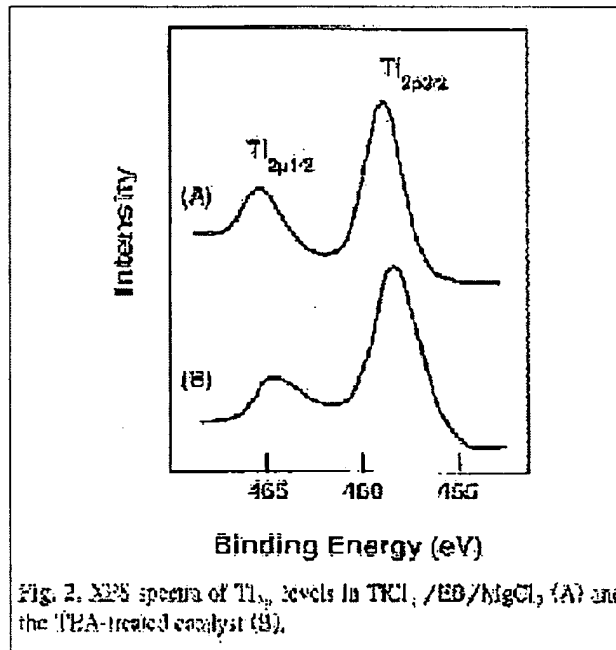


FIGURE 2 – Figure 2 from ref. 1

Examples 3 and 1 from Luciani I and Luciani II, respectively, have been reproduced and analyzed by XPS spectroscopy and compared to the catalyst from the present application, as shown in Table 1 hereinbelow. Since all the examples from this table use TEAL as cocatalyst during polymerization, the FWHM has been analyzed from them with or without the reaction with TEAL.

TABLE 1

CATALYST EXAMPLE	TEAL REACTION	BINDING ENERGY (Ti 2p 3/2)	FWHM (eV)
Example 1 Document Luciani II	NO	459.11	2.5
	YES	n.a.	3.6
Example 3 Document Luciani I	NO	459.01	2.7
	YES	n.a.	3.5
Example 8 - Present application	NO	458.65	3.0
	YES	n.a.	3.0

n.a. – not analyzed

As can be seen from Table 1, both examples from Luciani I and Luciani II show narrower FWHM, when compared to example 8 of the present application. After the reaction of all examples of Table 1 with TEAL, FWHM became larger (higher values) for both examples from Luciani I and Luciani II, when compared to example 8 of present application. The explanation is that the electron donor interacts with titanium and also magnesium sites and, after the reaction with TEAL, which can remove part of the donor, the environment around these sites is affected. Another evidence to prove that titanium species from examples 3 and 1 from Luciani I and Luciani II, respectively, are different in nature from those of catalyst example of the present application is the binding energy, as shown in Table 1. The difference in energy of titanium species is probably due to the presence of the electron donor used during the preparation of the catalysts from examples 3 and 1 from Luciani I and Luciani II, respectively.

Also from the XPS spectra, the intensity of the signals and the intensity ratio of the signals of elements such as C, Si, Ti and Mg were observed and analyzed, according to Table 2:

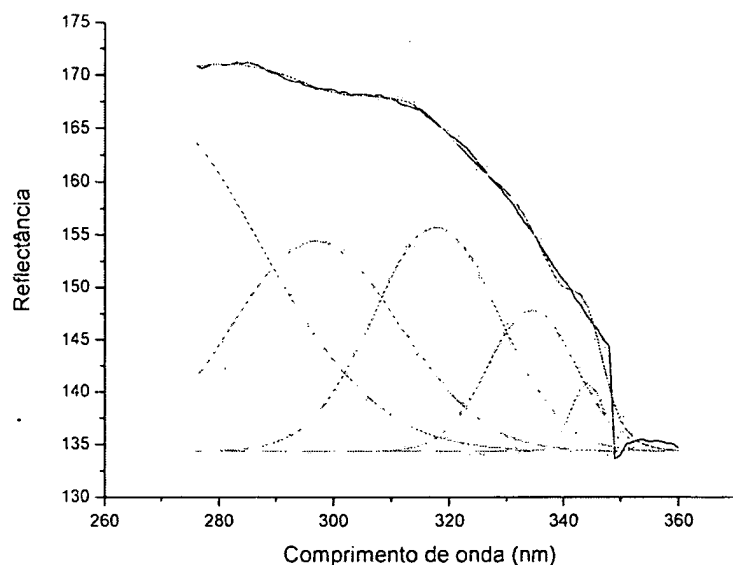
TABLE 2

	INTENSITY OF THE SIGNALS				INTENSITY RATIO OF THE SIGNALS		
	C 1s	Si 2p	Ti 2p 3/2	Mg KLL	Mg/Si	Ti/Si	Mg/Ti
Example 1 Document Luciani II	8100	3237	4251	4152	1,28	1,31	0,98
Example 3 Document Luciani I	5684	4868	3100	3278	0.67	0.64	1.06
Example 8 Present application	4300	5754	2350	1343	0.23	0.41	0.57

It may be observed in example 1 of Luciani II that there is much more Ti covering the catalytic support (silica) than the other examples (see Ti/Si ratio at table 1). The amount of Ti recovering the catalytic support of Example 8 of the present application is the lowest. It is also possible to conclude that the catalyst from Example 8 of the present application has the lowest amount of Mg covering the catalytic support.

Another way to demonstrate that the catalyst products are different, although they show the same elements in the composition (Ti, Mg, Si, Al), is through the analysis of UV-VIS diffuse reflectance for solids (DRS). With this analysis, it is possible to obtain information such as oxidation state, coordination sphere around the transition metal as well as quantitative aspects for assessing the concentrations of transition metal ions.

Thus, one of the catalysts examples from Luciani II (example 1) was analyzed by this technique in comparison with the catalyst of example 8 of the present application, as you will note in Figures 3a and 3b, where both spectra from the two catalysts were deconvoluted in order to identify the titanium species in the surface of the catalytic supports (see wave number values, titanium chemical species and their concentration at Table 3).



Data: Data1\_B  
Model: Gauss  
Equation:  $y = y_0 + \frac{A}{w \sqrt{\pi/2}} \exp(-2 * ((x - xc)/w)^2)$   
Weighting:  
y No weighting  
Chi^2/DoF = 1.02252  
R^2 = 0.99455

y0	134.34544	±1.77498
xc1	267.30288	±2565.70364
w1	40.36093	±6244.97958
A1	1630.39969	±366030.23953
xc2	296.90609	±1037.51745
w2	29.01646	±2635.49114
A2	729.95874	±316519.13048
xc3	317.7706	±172.97885
w3	21.87812	±220.69492
A3	586.27523	±38277.54729
xc4	334.45149	±13.77545
w4	15.35511	±22.25084
A4	260.35258	±2295.37699
xc5	344.18289	±0.37637
w5	5.7232	±1.60271
A5	47.091	±34.71853

FIGURE 3a - UV-VIS (DRS) spectra for catalyst from example 1 of Luciani II



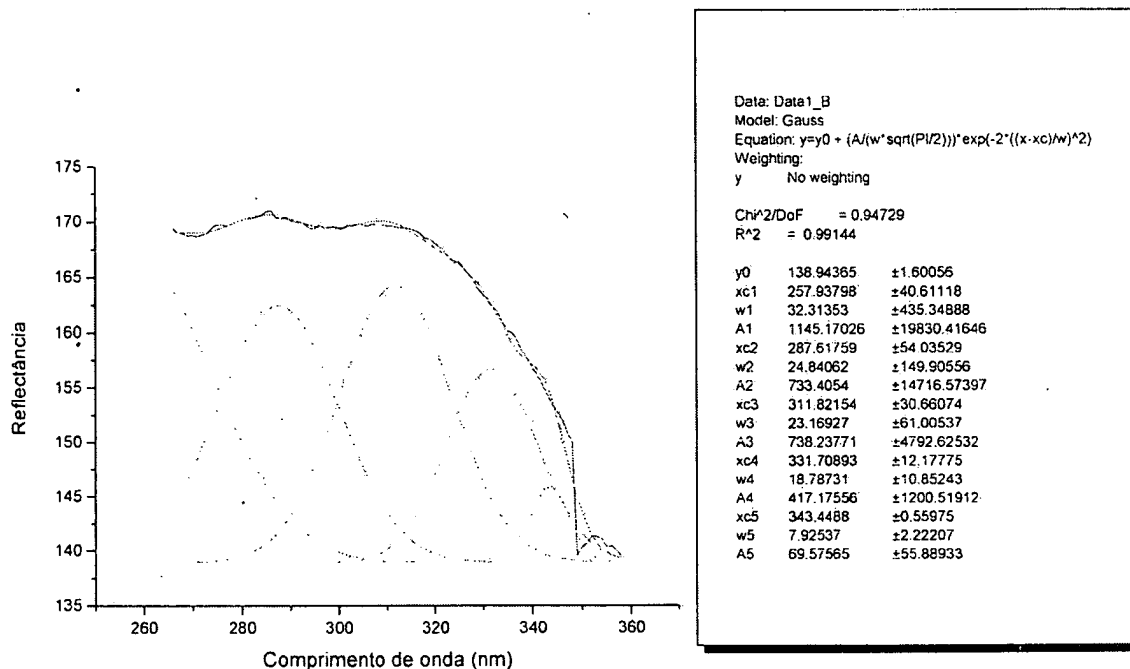


FIGURE 3b - UV-VIS (DRS) spectra for catalyst from example 8 of present application

TABLE 3

	Example 1 Document Luciani II					Example 8 Present application				
Wave number (nm)	267.3	296.9	317.8	334.5	344.2	257.9	287.6	311.8	331.7	343.4
Chemical species	Pentacoordinated Ti	Pentacoordinated Ti	Octahedral species of Ti (IV)	Oligomeric octahedral Ti (IV)	Oligomeric octahedral Ti (IV)	Pentacoordinated Ti	Pentacoordinated Ti	Oligomeric octahedral Ti (IV)	Oligomeric octahedral Ti (IV)	Oligomeric octahedral Ti (IV)
Concentration (%)	50.1	25.4	15.0	8.1	1.4	34.9	21.6	25.9	13.4	4.2

According to the literature, when the titanium and magnesium compounds are deposited over the catalytic support (silica), there is a precipitation of both compounds and the titanium compound is immobilized on the crystal faces (100) and (110) of  $MgCl_2$ . The crystal structure of  $MgCl_2$  is isotype to that of  $\gamma$ - $TiCl_3$  and therefore it offers the equivalent coordination site for immobilizing titanium alkyl halide complexes at the

MgCl<sub>2</sub> surface. The importance of the similarities in the structures and ionic radii of MgCl<sub>2</sub> and TiCl<sub>3</sub> or TiCl<sub>4</sub> was pointed out by Kasiwa [ref. 2] and Galli *et al* [ref. 3]. As pointed out by Busico and Corradini [ref. 4], the model of catalytic centers was resulted from the coordination of TiCl<sub>4</sub> units, subsequently reduced to TiCl<sub>3</sub> and alkylated by aluminum alkyl, to lateral unsaturated (100) and (110) faces of MgCl<sub>2</sub> crystals, as shown in Figure 3.

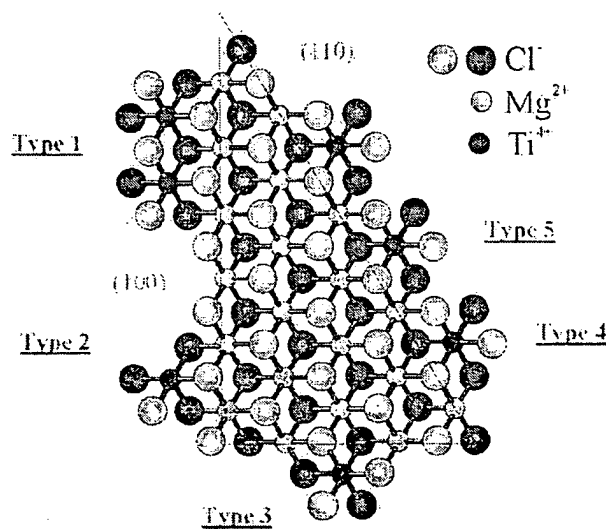


FIGURE 3 - Models for the coordination of TiCl<sub>4</sub> on MgCl<sub>2</sub>

Looking at Figure 3, it is possible to correlate the titanium sites form of this model to the chemical species showed by both catalysts products analyzed by UV-VIS and a resume thereof is at Table 4, below:

TABLE 4

Example 1 Document Luciani II						Example 8 Present application				
Wave number (nm)	267.3	296.9	317.8	334.5	344.2	257.9	287.6	311.8	331.7	343.4
Chemical species	Pentacoordinated Ti	Pentacoordinated Ti	Octahedric species of Ti (IV)	Oligomeric octahedric Ti (IV)	Oligomeric octahedric Ti (IV)	Pentacoordinated Ti	Pentacoordinated Ti	Oligomeric octahedric Ti (IV)	Oligomeric octahedric Ti (IV)	Oligomeric octahedric Ti (IV)
Geometry	Trigonal bipyramidal	Trigonal bipyramidal	Monomeric octahedral	oligomeric octahedral	oligomeric octahedral	Trigonal bipyramidal	Trigonal bipyramidal	oligomeric octahedral	oligomeric octahedral	oligomeric octahedral
Site Type (from Figure 3)	Type 2	Type 2	Types 3 and 4	Type 1	Type 1	Type 2	Type 2	Type 1	Type 1	Type 1

It can be verified from Tables 3 and 4 that the catalyst from the present application (example 8) shows two categories with different chemical species in the composition while catalyst from Luciani II (example 1) shows three categories with different chemical species in the composition. The spectra deconvolution from both catalysts indicates pentacoordinated Ti and oligomeric species of Ti (IV) at example 8 of the present application while the other spectrum shows pentacoordinated Ti, oligomeric species of Ti (IV) and also monomeric octahedral species of Ti (IV). Another point to be observed is that the concentration of each site on both catalysts is quite different from each other.

Under these aspects, it is demonstrated that the processes of catalyst preparation are distinct and the catalyst composition and the way that Mg and Ti compounds precipitate on the support, in the presence or not of the electron donor, affect the catalyst response when submitted to olefin copolymerization.

1 Mori, H. et al., *J. of Molecular Catalysis A: Chemical*, 1999, **140**, 165

2 Kashiwa, N., *Polym. J.*, 1980, **12**, 603.

3 Galli, P., Luciani L. and Cecchin, G., *Angew. Makromol. Chem.*, 1981, **94**, 63.

4 Corradini, P.; Barone, V.; Fusco, R.; Guerra, G. *Gazz. Chim. Ital.* 1983, **113**, 601-607.

For all of the above reasons which merely embellish upon all of the arguments previously presented, the Board of Appeals is respectfully requested to reverse the Examiner and allow all of the claims of the present application.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Joseph A. Kolasch Reg. No. 22,463 at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

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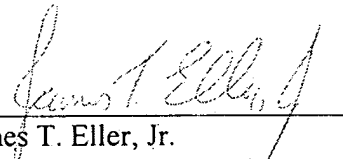
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If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37.C.F.R. §§1.16 or 1.147; particularly, extension of time fees.

Dated: June 30, 2009

Respectfully submitted,

By



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